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### Three-Dimensional Framework with Channeling Cavities for Small Molecules: $\{[\text{M}_2(4,4'\text{-bpy})_3(\text{NO}_3)_4]\cdot x\text{H}_2\text{O}\}_n$ ( $\text{M} = \text{Co}, \text{Ni}, \text{Zn}$ )\*\*

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The synthesis of coordination polymers with large channels or cavities is of great interest due to their intriguing structural diversity and their potential functions as microporous solids (including molecular adsorption, ion exchange, and heterogeneous catalysis).<sup>[1–10]</sup> The simple bis(monodentate) ligand 4,4'-bipyridine (4,4'-bpy) affords a variety of two- and three-dimensional frameworks when coordinated to various metal ions.  $\{[\text{Cd}(4,4'\text{-bpy})_2(\text{NO}_3)_2]\cdot (\text{C}_6\text{H}_4\text{Br}_2)_2\}_n$ ,<sup>[3]</sup>  $\{[\text{Zn}(4,4'\text{-bpy})_2]\text{SiF}_6\cdot x\text{DMF}\}_n$ ,<sup>[6]</sup> and  $\{[\text{Cu}(\text{cnge})_2\}_2(\mu\text{-}4,4'\text{-bpy})\}[\text{BF}_4]_2\cdot \text{MeCN}$  ( $\text{cnge} = 2\text{-cyanoguanidine}$ )<sup>[11]</sup> have assemblies of 2-D sheets, whereas  $\{[\text{Zn}(4,4'\text{-bpy})_2(\text{H}_2\text{O})_2]\text{SiF}_6\}_n$ ,<sup>[12]</sup>  $[\text{Cu}(4,4'\text{-bpy})\text{Cl}]_n$ ,<sup>[14]</sup>  $\{[\text{Cu}(4,4'\text{-bpy})_{1.5}\}\text{NO}_3(\text{H}_2\text{O})_{1.5}\}_n$ ,<sup>[17]</sup> and  $[\text{Ag}(4,4'\text{-bpy})\cdot \text{NO}_3]_n$ , have 3-D interpenetrating structures.<sup>[10]</sup> Although the number of coordination polymers with new structural aspects is increasing, compounds that reveal functional properties characteristic of their cavities and channels are still lacking. The anion-exchange capability of the silver compound is one of a few recent instances of such properties.<sup>[10]</sup>

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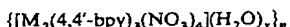
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Here we report the synthesis and crystal structures of novel coordination polymers **1–3**, which have large micropores and can adsorb small gaseous molecules such as  $\text{CH}_4$ ,  $\text{N}_2$ , and  $\text{O}_2$ .



**1:**  $\text{M} = \text{Co}$ ,  $x = 4$

**2:**  $\text{M} = \text{Ni}$ ,  $x = 4$

**3:**  $\text{M} = \text{Zn}$ ,  $x = 2$

Complexes **1–3** were prepared by the reaction of  $\text{M}(\text{NO}_3)_2\cdot x\text{H}_2\text{O}$  ( $\text{M} = \text{Co}, \text{Ni}, \text{Zn}$ ) with 4,4'-bpy in acetone/EtOH.<sup>[13]</sup> Complex **1** was characterized by X-ray crystallography, and the isomorphous structures of **1–3** were clearly demonstrated by their X-ray powder diffraction patterns.

Figure 1 shows the coordination around the Co center of **1** and the crystal structure along the *c* axis. The three nitrogen

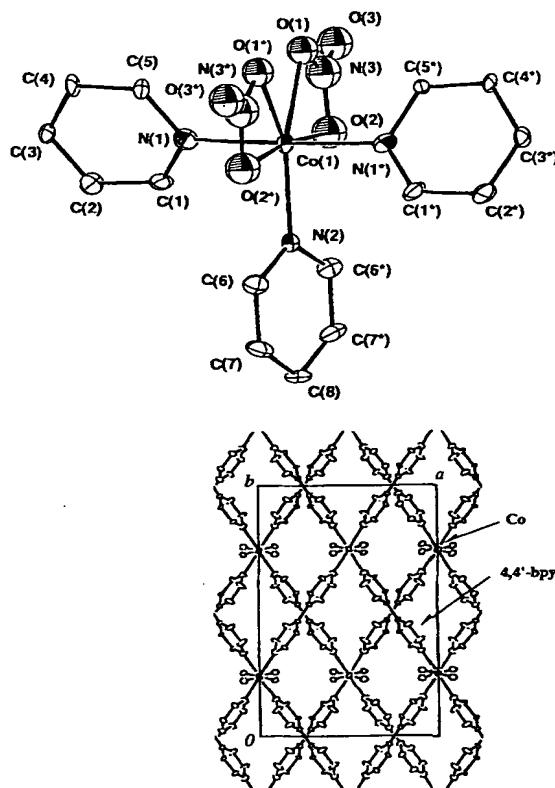
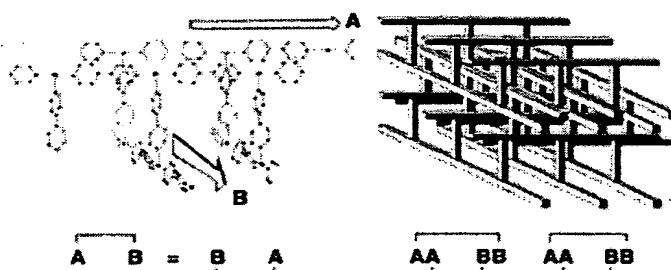


Figure 1. Top: ORTEP drawing of **1** around the Co center (ellipsoids at 20% probability); the hydrogen atoms are omitted for clarity. Selected bond distances [ $\text{\AA}$ ] and angles [ $^\circ$ ]:  $\text{Co}(1)-\text{N}(1)$  2.13(1),  $\text{Co}(1)-\text{N}(2)$  2.13(2),  $\text{Co}(1)-\text{O}(1)$  2.23(1),  $\text{Co}(1)-\text{O}(2)$  2.32(1);  $\text{N}(1)-\text{Co}(1)-\text{N}(1^*)$  178.2(8),  $\text{N}(1)-\text{Co}(1)-\text{N}(2)$  90.9(4),  $\text{N}(1)-\text{Co}(1)-\text{O}(1)$  84.5(5),  $\text{N}(1)-\text{Co}(1)-\text{O}(1^*)$  94.1(5),  $\text{N}(1)-\text{Co}(1)-\text{O}(2)$  85.8(5),  $\text{N}(1)-\text{Co}(1)-\text{O}(2^*)$  94.3(5),  $\text{N}(2)-\text{Co}(1)-\text{O}(1)$  140.8(4),  $\text{N}(2)-\text{Co}(1)-\text{O}(1^*)$  140.8(4),  $\text{N}(2)-\text{Co}(1)-\text{O}(2)$  86.1(4),  $\text{N}(2)-\text{Co}(1)-\text{O}(2^*)$  86.1(4),  $\text{O}(1)-\text{Co}(1)-\text{O}(1^*)$  78.5(7),  $\text{O}(1)-\text{Co}(1)-\text{O}(2)$  54.7(5),  $\text{O}(1)-\text{Co}(1)-\text{O}(2^*)$  133.1(6),  $\text{O}(2)-\text{Co}(1)-\text{O}(2^*)$  172.2(8). Bottom: View of the crystal structure of **1** along the *c* axis; the hydrogen atoms and nitrate anions are omitted for clarity.

atoms from the two 4,4'-bpy molecules and the four oxygen atoms from the two nitrate anions form a distorted pentagonal bipyramidal around the  $\text{Co}^{II}$  atom;  $\text{N}(1)$  and  $\text{N}(1^*)$  are in the axial positions. The  $\text{Co}^{II}$  centers are bridged by 4,4'-bpy to afford infinite 1-D chains in the *ab* plane in which the pyridine rings of the 4,4'-bpy units are twisted by  $38.2^\circ$  with respect to each other. The chains are separated by about  $10.0 \text{ \AA}$ . Two sets of arrays are

observed for the 1-D chains. In one the chains are oriented at an angle of  $54.8^\circ$  to the  $a$  axis, and in the other at angle of  $-54.8^\circ$ . The two planes that correspond to the two types of chains are designated A and B (left side of Scheme 1). The distinct planes are bound over 4,4'-bpy bridges along the  $c$  axis to form a double-sheet structure. The pyridine rings of the bridging 4,4'-bpy molecules are twisted by about  $41.5^\circ$ . Hence, each 1-D chain on the A and B planes is sterically fixed by the 4,4'-bpy unit, which acts as a pillar.



Scheme 1. Formation of the crystal structure of 1. A section of the 3-D basic unit made up of planes A and B is shown on the left, and the result of their assembly on the right.

The assembly of these basic units is shown schematically in Scheme 1. The most characteristic feature of the resulting structure can be described as a tongue-and-groove structure (Scheme 1, right). To the best of our knowledge this type of assembly has not yet been observed in the 3-D frameworks of coordination polymers with 4,4'-bpy bridges.

The interplanar distance between A and B in the 3-D basic unit is about  $11.3\text{ \AA}$ . The nonlinked adjacent planes are separated by about  $2.6\text{ \AA}$  (A/A, B/B) and about  $6.1\text{ \AA}$  (A/B). The relatively large distance between the adjacent A and B planes creates channeling cavities along the  $a$  and  $b$  axes with dimensions of about  $3 \times 6$  and  $3 \times 3\text{ \AA}$ , respectively. These channeling cavities are occupied by water molecules, which show no significant binding interactions with the crystal framework.

The unique 3-D structures of 1–3 with channeling cavities prompted us to examine their gas-adsorption properties, one of the most attractive functions of microporous solids.<sup>[4, 14–16]</sup> Figure 2 shows the results of the adsorption–activity experi-

ments of anhydrous 1, obtained by drying under vacuum, with  $\text{CH}_4$ ,  $\text{N}_2$ , and  $\text{O}_2$ . Rapid increase in the amount of adsorbed gases is shown by the increase in pressure up to 5 atm; this indicates diffusion of the gases into the cavities.<sup>[17]</sup> X-ray powder diffraction patterns confirm that there is no structural decomposition upon removal of crystal waters. Moreover, adsorption and desorption experiments with  $\text{CH}_4$  provide the same isotherm (Figure 2), which means that there is no deformation of the crystal framework upon adsorption. The isotherms are of type I according to the IUPAC classification.<sup>[18]</sup> About 2.3 mmol of  $\text{CH}_4$  and 0.80 mmol of  $\text{N}_2$  or  $\text{O}_2$  are adsorbed per 1.0 g of the anhydrous sample at a pressure of 30 atm.

An investigation of the adsorption capabilities of zeolites for several gases ( $\text{CH}_4$ ,  $\text{N}_2$ ,  $\text{CO}_2$ , Ar, Kr, and Xe) showed that gas affinity corresponds to cavity size.<sup>[14, 15, 19–22]</sup> Zeolites 13X and 5A show a high affinity for gases<sup>[23]</sup> and have channel dimensions of  $7.4 \times 7.4\text{ \AA}$  and  $4.1 \times 4.1\text{ \AA}$ , respectively, which are similar to those of 1–3. In addition to structural dimensions, the specific interaction of organometallic cavity frameworks with adsorbed molecules could be controlled in the coordination polymers, which might lead to new types of adsorption properties.

#### Experimental Section

**1:** 4,4'-Bipyridine (0.82 g, 5.25 mmol) in EtOH (50 mL) was added to a solution of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (0.68 g, 2.33 mmol) in acetone (50 mL), and the mixture allowed to stand for one week. The red microcrystals obtained were collected by filtration and dried in vacuo for 2 h. Elemental analysis calcd for  $\text{C}_{30}\text{H}_{24}\text{N}_{10}\text{O}_{16}$ : C 39.75, H 3.56, N 15.45; found: C 40.58, H 2.98, N 15.45; IR (KBr):  $\bar{\nu}$  [ $\text{cm}^{-1}$ ] = 3375 (br), 1609 (s), 1536 (m), 1466 (s), 1414 (s), 1296 (s), 1219 (m), 1067 (s), 1032 (m), 1009 (m), 880 (w), 861 (w), 814 (s), 733 (m), 635 (s), 573 (m), 505 (m).

Complexes 2 and 3 were prepared analogously. **2:** Elemental analysis calcd for  $\text{C}_{30}\text{H}_{32}\text{N}_{10}\text{NiO}_{16}$ : C 39.77, H 3.56, N 15.46; found: C 41.18, H 3.08, N 15.30; IR (KBr):  $\bar{\nu}$  [ $\text{cm}^{-1}$ ] = 3385 (br), 1537 (m), 1537 (m), 1494 (s), 1427 (m), 1385 (w), 1302 (s), 1224 (m), 1076 (m), 1047 (w), 1012 (m), 815 (m), 734 (w), 638 (m), 575 (w), 527 (w). **3:** Elemental analysis calcd for  $\text{C}_{30}\text{H}_{28}\text{N}_{10}\text{O}_{14}\text{Zn}_2$ : C 40.79, H 3.19, N 15.86; found: C 40.43, H 2.83, N 15.78; IR (KBr):  $\bar{\nu}$  [ $\text{cm}^{-1}$ ] = 3406 (br), 1763 (w), 1612 (s), 1537 (m), 1415 (br), 1294 (m), 1219 (m), 1070 (m), 1030 (s), 1012 (m), 985 (w), 861 (w), 812 (s), 731 (m), 638 (m), 574 (m), 507 (m).

X-ray structure determination of 1: All data were measured on a Rigaku AFC7R diffractometer with graphite-monochromated  $\text{Mo}_{\text{K}\alpha}$  radiation and a rotating-anode generator (12 kW). The unit-cell constant was obtained from a least-squares refinement of 25 carefully centered reflections with  $2\theta$  values between  $8.04$  and  $18.75^\circ$ . The structure was solved by direct methods and refined by the block-diagonal least-squares method. Hydrogen atoms except for those of water molecules were placed at calculated positions, but their parameters were not refined. The final refinements were carried out with full-matrix least-squares techniques for non-hydrogen atoms. All calculations were performed with the TEXSAN crystallographic software package (Molecular Structure Corporation). Crystal data:  $\text{C}_{30}\text{H}_{32}\text{N}_{10}\text{CoO}_{16}$ ,  $M_r = 906.51$ , orthorhombic, space group  $Cc\bar{c}a$ ,  $a = 12.267(7)$ ,  $b = 19.025(7)$ ,  $c = 17.412(4)\text{ \AA}$ ,  $V = 4063(2)\text{ \AA}^3$ ,  $Z = 4$ ,  $\rho_{\text{calcd}} = 1.482\text{ g cm}^{-3}$ ,  $\lambda(\text{Mo}_{\text{K}\alpha}) = 0.71069\text{ \AA}$ ,  $F(000) = 1836$ ,  $\mu(\text{Mo}_{\text{K}\alpha}) = 8.96\text{ cm}^{-1}$ ,  $T = 25^\circ\text{C}$ ,  $2\theta_{\text{max}} = 55.2^\circ$ , of 2324 reflections measured 528 were observed ( $I > 2.00\sigma(I)$ ), 108 parameters;  $R = 0.086$ ,  $R_w = 0.095$ . Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100382. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: int. code + (1223) 336-033; e-mail: deposit@chemcrys.cam.ac.uk).

Gas-adsorption measurements for 1: The adsorption isotherms of  $\text{CH}_4$ ,  $\text{N}_2$ , and  $\text{O}_2$  were measured by reported procedures [14, 15]. The apparatus was equipped with a Cahn R-100 electrobalance contained within a SUS steel pressure chamber that was connected with two separate lines for evacuation and adsorbate gas pressurization. Prior to adsorption measurement, to remove the solvated waters, 1 (63.1 mg, 0.074 mmol) was dried under reduced pressure at  $25^\circ\text{C}$  until additional weight loss was not observed. The adsorbate gases ( $\text{CH}_4$ ,  $\text{N}_2$ ,  $\text{O}_2$ ) were dosed into the adsorption chamber, then the change of the weight of the sample was monitored. The entire adsorption isotherms were determined by increasing the adsorbate gas pressure to a maximum of 36 atm. Gas-adsorption measurements for 2 and 3 were carried out by a similar procedure. The desorption isotherm was also obtained for  $\text{CH}_4$  adsorption on 1.

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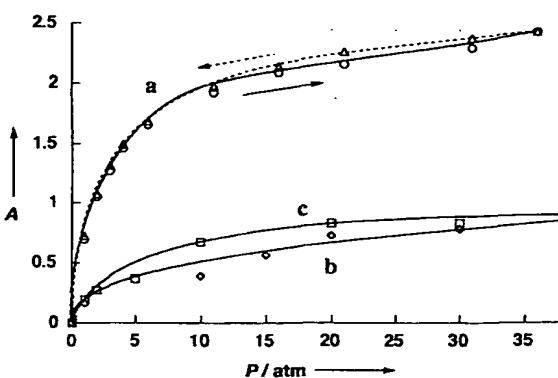


Figure 2. Isotherms for the adsorption of  $\text{CH}_4$  (a),  $\text{N}_2$  (b), and  $\text{O}_2$  (c) on 1 at 298 K in the range of 1–36 atm;  $A$  = absolute adsorption in mmol of adsorbed gas per gram of anhydrous sample. In the case of  $\text{CH}_4$  gas desorption (triangles) was carried out directly after gas adsorption (circles). Since the two isotherms are nearly identical, one can conclude that there is no structural change of the channels during gas adsorption.

**Keywords:** cobalt • crystal engineering • inclusion compounds • microporosity • N ligands

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## A Bis(carceplex) from a Cyclic Tetramer of Cavitands\*\*

Naveen Chopra and John C. Sherman\*

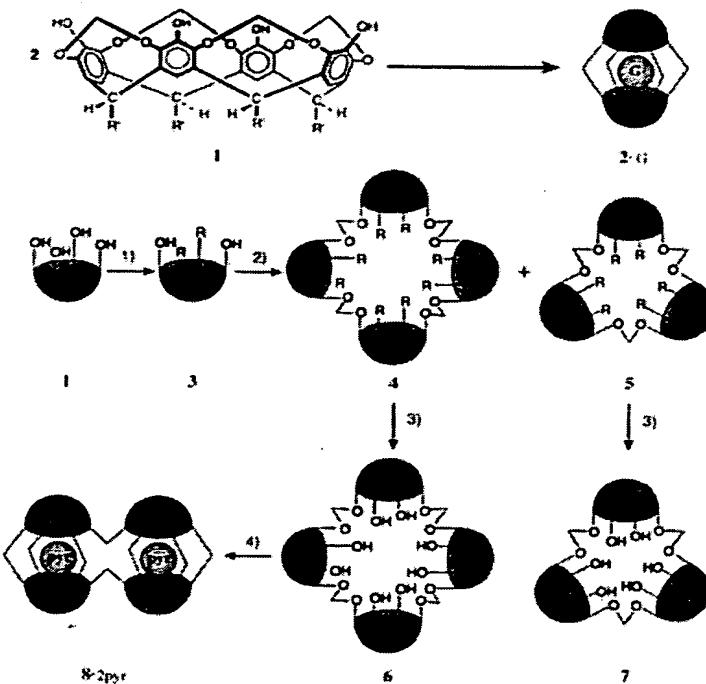
One of the key goals of supramolecular chemistry is the construction of complex molecular assemblies that are composed of simple subunits or building blocks. The formation of supramolecular assemblies is common in nature and materials science, as exemplified by the braid-like structure of collagen<sup>[1]</sup> and the controlled design and engineering of crystal lattices.<sup>[2]</sup> To construct de novo assemblies of such complexity, it is pru-

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dent to use highly rigid building blocks and to seek means that limit the ways in which these units can be assembled.<sup>[3]</sup> Here we demonstrate the use of cavitands—rigid macrocycles that contain an enforced cavity—to form new, complex assemblies, most notably the first “bis(carceplex)”.

It has been known for some time that two bowl-shaped molecules, cavitands or “bowls”, can be linked in the presence of a suitable guest molecule to yield a closed-surface molecule, a carceplex. The guest is permanently incarcerated within the newly formed shell, akin to a ship in a bottle.<sup>[4]</sup> We studied the effects of guests as templates in the synthesis of carceplexes,<sup>[5]</sup> and found that formation of carceplex **2·G** (**G** = guest) is subject to a template effect that ranges one million fold. Moreover, the yields of **2·G** are as high as 87%. The formation of **2·G** demonstrates the efficient linkage of two cavitands to form a single, relatively small, closed-surface capsule (Scheme 1).



Scheme 1. Preparation of **3–8**. The bowls of carceplex **2·G** and bis(carceplex) **8·2·pyr** are linked through  $\text{OCH}_2\text{O}$  groups.  $R = \text{OCH}_2\text{C}_6\text{H}_5$ ;  $R' = \text{CH}_2\text{CH}_2\text{C}_6\text{H}_5$ ; 1)  $\text{PhCH}_2\text{Br}$ ,  $\text{K}_2\text{CO}_3$ , DMF, 6% yield of 3. 2)  $\text{CH}_2\text{BrCl}$ ,  $\text{K}_2\text{CO}_3$ , DMF, 15% yield of 4, 5% yield of 5. 3)  $\text{H}_2$ ,  $\text{Pd/C}$ , 4 atm, 94% yield of 6 (based on 4), 90% yield of 7 (based on 5). 4)  $\text{CH}_2\text{BrCl}$ ,  $\text{K}_2\text{CO}_3$ , *N*-methylpyrrolidinone, pyrazine, 74% yield of **8·2·pyr**.

Is it possible to link three or more cavitands to yield larger and/or more complex supramolecular assemblies? We report here the preparation of the first cyclic tetramer and cyclic trimer of cavitands,<sup>[6]</sup> which are potentially novel host molecules and precursors for new host molecules. To illustrate the potential of these cyclic oligomers, we also report the first bis(carceplex), which was prepared from the tetramer.

Tetrol **1** is the starting material for carceplex **2·G** and can be easily prepared in multi-gram quantities.<sup>[7]</sup> To efficiently link three or more cavitands in a cyclic array, one must limit the number of reactive sites on **1** and preclude formation of **2·G**. Both can be achieved by protecting two OH groups on opposing sides of **1**. We chose benzyl as the protecting group because of its size (it is large enough to inhibit carceplex formation), stability (the linkage remains intact upon subsequent acetal forma-